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Final Technical Report
on
The Development of Silicon Carbide Based
Hydrogen and Hydrocarbon Sensors

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Lewis Research Center
NASA, Cleveland, Ohio 44135

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Electronics Design Center
and
Edison Sensor Technology Center
Case Western Reserve University
Cleveland, Ohio 44106


Chung-Chiun Liu
Principal Investigator

Executive Summary

Silicon carbide is a high temperature electronic material. Its potential for development of chemical sensors in a high temperature environment has not been explored. The objective of this study is to use silicon carbide as the substrate material for the construction of chemical sensors for high temperature applications. Sensors for the detection of hydrogen and hydrocarbon are developed in this program under the auspices of Lewis Research Center, NASA. Metal-semiconductor or metal-insulator-semiconductor structures are used in this development. Specifically, using palladium-silicon carbide Schottky diodes as gas sensors in the temperature range of 100 to 400°C are designed, fabricated and assessed. The effect of heat treatment on the Pd-SiC Schottky diode is examined. Operation of the sensors at 400°C demonstrate sensitivity of the sensor to hydrogen and hydrocarbons. Substantial progress has been made in this study and we believe that the Pd-SiC Schottky diode has potential as a hydrogen and hydrocarbon sensor over a wide range of temperatures. However, the long term stability and operational life of the sensor need to be assessed. This aspect is an important part of our future continuing investigation.

Introduction

Detection of hydrogen and hydrocarbon over a wide range of concentration at relatively high temperature is important for many aerospace and commercial applications. This is due to their use as a fuel and their presence as a product of the fuel. The monitoring of flammable or explosive levels of the concentration of these gases is important. Detection of these gases at low concentrations is recognized as a vital issue in controlling and

monitoring emissions from, for instance, an aircraft engine. However, this is an environment of relatively high temperature and any sensing device must be able to survive and function in that environment. Silicon carbide, SiC, is an electronic material suitable for high temperature applications; however, its potential as a high temperature gas sensor material has not been explored. There are significant advantages of gas sensing using SiC as the semiconductor rather than silicon, Si. These advantages are the improved material properties of SiC over Si at high temperatures, superior mechanical strength, and enhanced thermal conductivity. This improved thermal conductivity is an advantage for fast heating of the sensor. The detection of hydrocarbons which require decomposition at high temperature can also be facilitated by heating the sensor at a high temperature without excess amount of thermal energy.

Under the auspices of Lewis Research Center, NASA, we have explored the capability of SiC for gas sensing, particularly for hydrogen and hydrocarbon initially. A Schottky diode composed of palladium, Pd, and palladium-silver, Pd-Ag, gate layer deposited on SiC has been shown sensitivity to hydrogen at 5000 ppm in an inert gas environment at near room temperature [1-2]. Silicon carbide based capacitors using platinum as the gas sensitive film has shown a sensitivity to hydrogen gas as low as 2.5 ppm and have been operated at temperatures as high as 800°C [3]. Also, sensitivity to hydrocarbons such as methane, ethane and propane at 457°C has been demonstrated [4]. Fabrication of SiC-based sensor with an integrated heater and temperature detector has been attempted with some degree of success [1].

A possible mechanism for hydrogen and hydrocarbon detection in SiC-based devices using Pd is similar to that proposed for Pd/Si based sensors: the dissociation of hydrogen or hydrocarbons on the palladium metal surface results in the formation of a dipole layer composed of hydrogen at the metal-semiconductor or metal-insulator interface. This dipole layer can affect the electronic properties of the device in proportion to the quantity of hydrogen and other gaseous species in the surrounding environment.

In our research, SiC-based sensors for the detection of hydrogen and hydrocarbons operating at least 400°C are being developed. Our effort focuses on the fabrication of a sensor prototype which can withstand high temperature operation and be sensitive to hydrogen related gases in a variety of ambients. The sensing element will be Pd or Pd-alloy as the sensing gate material. It is recognized that a complete sensor package needs to be developed for evaluation of the sensor's performance, and this effort will be mainly carried out by the researchers at Lewis Research Center, NASA.

We have an excellent working relationship with the researchers at NASA and substantial progress has been made on this research and development endeavor. We anticipate continued success and meaningful contributions will be made in the forthcoming year.

Research and Development Efforts

The palladium metal-semiconductor Schottky diodes using SiC as the semiconductor were prepared in this study. A 4H silicon-faced SiC substrate was used, and a 4-5 μm thick 4H-SiC epilayer was grown by chemical vapor deposition. This prepared SiC substrate was provided by the researchers at Lewis Research Center, NASA. Approximately 400 angstroms of palladium metal were deposited onto the as-grown SiC epilayer surface using the ion beam coating technique. A circular Pd Schottky pattern with a diameter of 200 μm was used and the definition of the pattern was accomplished using the lift-off technique. A layer of palladium film was also deposited onto the backside of the substrate as a backside contact. However, due to the growth method of the substrate, the backside was often relatively rough. Thus, a means to smooth the surface of the backside of the substrate was necessary prior to any deposition of the palladium film for a good contact. This was accomplished by either mechanical polishing with fine alumina powder or an additional deposition of a thin layer of glass, silicon oxide, etc. to ensure the smoothness of the surface area of the backside of the substrate. A platinum thin film resistance type heater and temperature detector were also formed at the surrounding area of the sensor.

The use of Pd in an electronic structure with SiC as the semiconductor for gas detection for aerospace and other potential civilian applications depends on the inherent stability of Pd and SiC in a wide range of temperatures and ambient gas environments. The simplest structure for such applications will be a Pd-SiC Schottky diode although an interaction between Pd directly deposited on SiC can be expected even at room temperature [5]. The effect of this interaction on the gas sensing capability of such a device has not been explored. Also, it is necessary to determine the performance of such a sensor at high temperature and different temperature treatments of the gate layer. The long term stability of the sensor prototype in an important aspect which may be affected by the properties of the interface layer between Pd and SiC. Consequently, it may be necessary to produce a barrier layer between the Pd and SiC to stabilize the diode. The thickness and type of barrier layer will have to be examined experimentally. In this study, the temperature range was at 100 and at 400°C.

The evaluations of the sensor prototype were carried out mostly at Lewis Research Center, NASA. The test results were then used for modification of the sensor design and fabrication. Thus, selected test results are reported here to provide information on the characteristics of the developing sensor prototype.

For evaluation at 100°C, the sensor was first heated from 100°C to 200°C in air for 18 hours, then cooled back to 100°C. The sensor was then characterized at 100°C by exposure to different ambient gases. Figure 1 shows the capacitance characteristics of the sensor diode in air, helium and a helium-hydrogen (He-H₂) mixture. When exposed to the He-H₂ mixture the diode shows good response to hydrogen at a low concentration. Figure 2 shows the time-dependent capacitance response of the diode sensor to the gases both before heating treatment and after the final 400°C heat treatment. The two curves are very similar with the difference of a 0.5 pF in the capacitance at zero bias and heat treatment. It also shows that the recovery time towards the baseline is more rapid in air

than in He for both before and after the heat treatment. Thus, the heat treatment shifts the baseline capacitance of the diode but does not change the overall response of the diode

A summary of the results of the barrier height measurements for all temperatures and C-V measurements is given in Figure 3. The data points at 100°C represent the initial values. The data points at 200, 300 and 400°C represent the barrier heights measured at 100°C after temperature cycling to 200°C, 300°C and 400°C respectively.

Two observations can be made from the results in Figure 3. First, at a given temperature, the barrier heights measured in the He/H₂ mix are generally consistent with the exception of the first point at 300°C, and we believe that this is an experimental error. The results also suggest that after the heat treatment, the diode in air is in a different state than it is after exposure to the He/H₂ mix.

Secondly, after the first exposure to hydrogen, the subsequent barrier height measurements do not show a discernable pattern with respect to heat treatments. For example, the barrier heights do not consistently drift upward with temperature cycling. The experimental results also suggest that within the limits of this study, the long term diode structure as measured by the barrier height does not change drastically with heat treatment but rather seems to oscillate around a mean value.

This conclusion can be drawn from this preliminary study is that the heat treatment of a Pd-SiC diode at high temperature does not significantly change its ability to operate as a hydrogen sensor at 100°C. The formation of the interfacial layers between the Pd and SiC (presumably palladium silicides) and annealing within the SiC that have occurred with heating have shifted the baseline capacitance and slope of the $1/C^2$ versus V curves. However, the results of this work suggest that significant features of the diodes performance such as the form of the C-t curves, the difference between the air and He/H₂ mix capacitances, and the barrier height in the He/H₂ mix do not significantly change with heat treatment. This is important for the use of the diode as a sensor for it allows

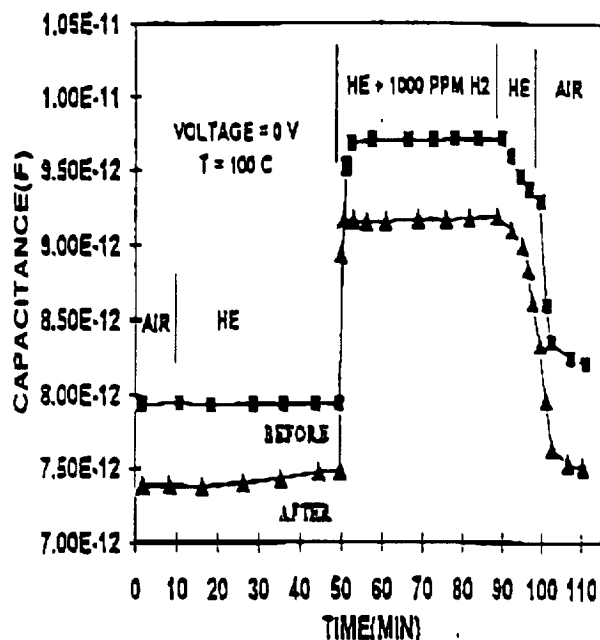


Figure 1. Capacitance at zero bias vs time at 100 °C before heat treating (■) and after the final heat treatment to 400 °C (▲). The diode is exposed to air, He, He + 1000 ppm H₂ then He and air. Heat treating does not significantly change the qualitative response of the diode.

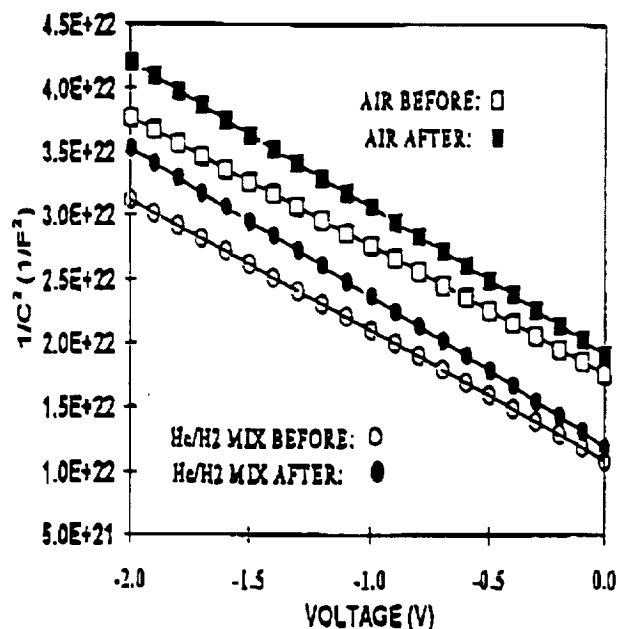


Figure 2. Plot of $1/C^2$ measured at 100 °C vs Voltage before heat treating in air (□) and He + 1000 ppm H₂ (○) and after heat treating in air (■) and He + 1000 ppm H₂ (●). A change with heat treating is evident in both the magnitude of the capacitance and slope of $1/C^2$.

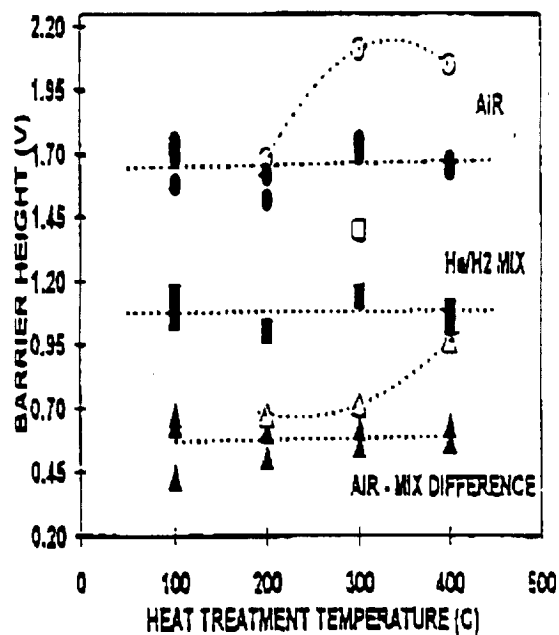


Figure 3. Barrier height measured at 100 °C by $1/C^2$ vs V measurements vs maximum heat treatment temperature. The open symbols are barrier heights first taken after air heat treatment: measured in air (○), measured in He + 1000 ppm H₂ (□), and the difference between these two barrier heights (Δ). The closed symbols are the barrier heights taken subsequently: measured in air (●), measured in He + 1000 ppm H₂ (■), and the difference between these two barrier heights (▲). The dotted lines are separate least squares fits through the closed and open symbols.

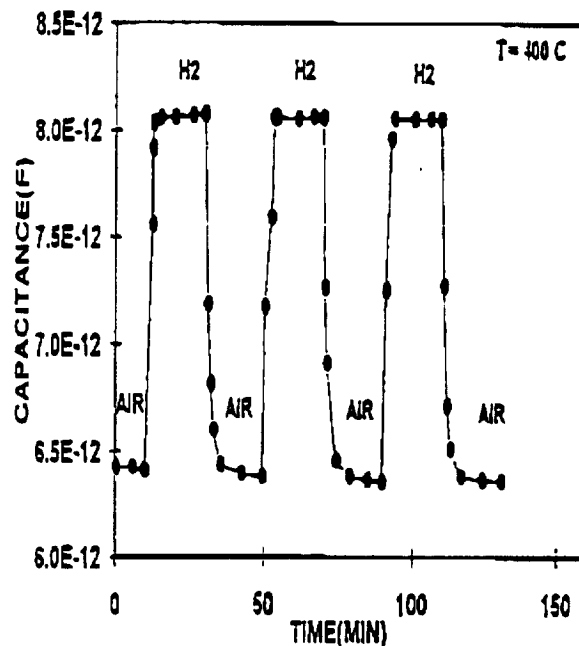


Figure 4. The capacitive response at zero bias of a Pd-SiC Schottky diode operated at 400 °C to cycles of air then 1000 ppm H₂ in N₂. The diode's response is significant and repeatable.

recalibration if needed after heating. However, the long-term stability of the sensor requires further assessment.

The performance characteristics of the diode at 400°C were also evaluated. Figure 4 shows the capacitive response at zero bias of a Pd-DiC Schottky diode operated at 400°C to cycles of air and 1000 ppm H₂ and N₂. The sensor shows good response to low levels of hydrogen and the response and recovery times are on the order of the time the chamber requires to reach steady state. The difference in the corresponding barrier height as measured by $1/C^2$ versus V in air and in the N₂/H₂ mix are on the order of several hundred millivolts. This also indicates that the response of this MS system to low concentrations of hydrogen is sufficient to be used in a MOSFET configuration or be observed by measuring the current.

The response of the sensor measured using the forward current of the diode at +0.9V is shown in Figure 5. The insert of Figure 5 shows the same testing data but in a logarithmic scale. Briefly stated, these preliminary results show that the Pd-SiC Schottky diode has potential as a highly sensitive hydrogen sensor.

The detection of hydrocarbon using the Pd-SiC Schottky diode at 400°C is shown in Figure 6 on a separate diode on the same Pd-SiC chip. The sensor was exposed to 300 ppm hydrogen in nitrogen, 300 ppm propylene in nitrogen and 300 ppm propylene and 1% O₂ in nitrogen. The response of the diode to hydrogen at 400°C is similar to that at 100°C. In both cases, the capacitance slightly increases in an inert environment, and significantly when exposed to H₂.

The exposure of the diode to hydrocarbon shows that the diode is sensitive to the hydrocarbon. Also, the sensor output decreases as the mixture changes from hydrogen to propylene. This decrease in signal may be due to incomplete dissociation of the hydrocarbon leading to less hydrogen available to migrate to the interface. It is also recognized that the baseline capacitance decreased after the exposure to propylene in

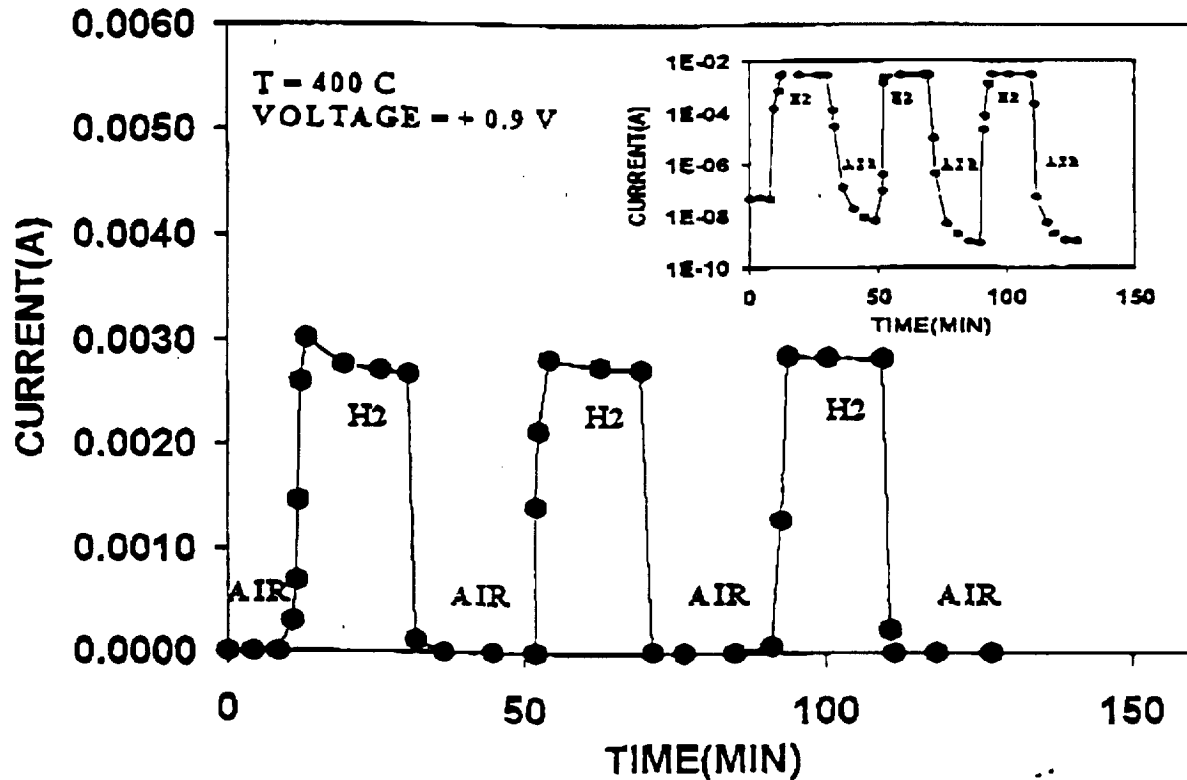


Figure 5. Response of the forward current at +0.9 V of a Pd-SiC Schottky diode operated at 400 C to 3 cycles of air followed by 1000 ppm of H₂ in N₂. The inset shows the same data in a logarithmic scale. The diode forward current changes by more than a factor of 1000 upon exposure to 1000 ppm hydrogen.

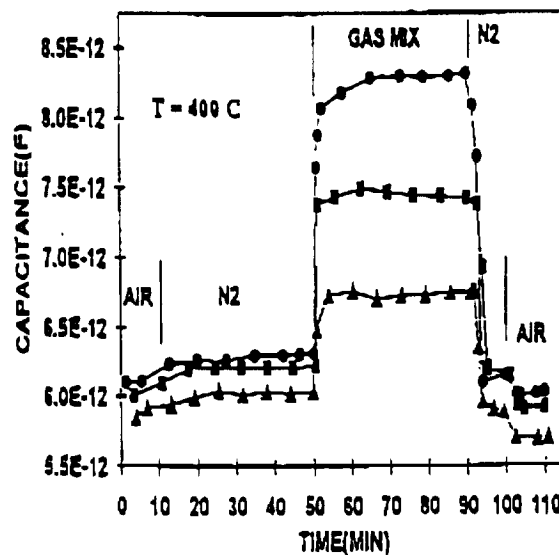


Figure 6. Capacitance vs time at 400 °C upon exposure to nitrogen plus 300 ppm of hydrogen (●) or propylene (■), or nitrogen plus 300 ppm propylene plus 1% O₂ (▲). The diode is first exposed to air, nitrogen then the hydrogen bearing gas mixture followed by nitrogen then air.

nitrogen. The reason for this change and its repeatability will be further investigated in the near future.

The package of the developing sensor is an ongoing research effort of this program. Modifications of the sensor heater to allow heating the SiC sensor to a high temperature are needed.

Summary

Fabrication of Pd-SiC Schottky diode sensors has been successfully carried out in this study. Evaluation of the sensor prototype at 100°C and 400°C were performed, and the capability of the sensor to sense hydrogen and hydrocarbon (propylene) at 400°C was demonstrated. Continued development of SiC-based sensors is planned. Further studies will determine the long term stability of the sensor at high temperatures. In particular, it will be determined if a barrier layer is needed for the Pd and the SiC interface. This study shows that the Pd-SiC sensor has potential for aerospace and commercial application.

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